

CHEMICAL VAPOUR DEPOSITION AND CHARACTERISATION OF ZnO NANOSTRUCTURES FOR CO GAS SENSING APPLICATION

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By

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CERTIFICATE

This is to certify that the work incorporated in this thesis entitled "**Chemical Vapour Deposition and Characterisation of ZnO nanostructures for CO gas sensing application**" submitted to Central University of Jharkhand, Ranchi Campus for the award of degree of Integrated Masters of Technology in Energy Engineering has been carried out by **Mr. Indranil Halder** under the supervision of **Dr. M. Senthil Kumar and Dr. Preetam Singh at CSIR-National Physical Laboratory, New Delhi** from June 2018 to May 2019.

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Abbreviations

SAW	Surface Acoustic Wave
SEM	Scanning Electron Microscope
FESEM	Field Emission Scanning Electron Microscope
EDX	Energy Dispersive X-ray Analysis
XRD	X-Ray Diffraction
Arb. Unit	Arbitrary unit
PL	Photo Luminescence
MOS	Metal Oxide Semi-conductor
sccm	Standard Cubic Centimetre per Minute
LPM	Litre per Minute
ZnO	Zinc Oxide
CVD	Chemical Vapour Deposition
PID	Proportional, Integral, and Derivative
NBE	Near Band Edge
UV	Ultra-Violet
FWHM	Full Width at Half Maximum

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Abstract

Metal oxide semiconductors have seen significant advancements in recent days for gas sensing applications, to detect the toxic gases, flammable gases etc. in household, industry and other locality areas. There are many physical and chemical vapour deposition processes available for the preparation of metal oxide thin films and nanostructures. In this work, thermal chemical vapour deposition technique has been employed to deposit ZnO nanostructured films on various substrates such as alumina, sapphire and silicon substrates. Pure Zn powder was used as precursor and was oxidised to form ZnO. Different types of ZnO nanostructures have been obtained by varying the deposition temperature under a controlled oxygen gas flow condition. The structure, morphological and optical properties of prepared ZnO nanostructures were characterized using x-ray diffraction, field emission scanning electron microscopy, energy dispersive x-ray analysis, Raman scattering and photoluminescence techniques. It is found that the ZnO has crystallized in hexagonal structure and has good structural and optical emission properties. Various nanostructures such as star-nanoneedle shape, nanorod network structure and vertically aligned nanorod array are formed depending on deposition temperature and substrates used. An intense band-edge UV emission along with a weak defect band as observed in photoluminescence spectrum reveals the high structure and optical quality of the deposited ZnO nanostructures.

The gas sensing characteristics of thermal CVD grown ZnO nanostructures have been investigated for the target air pollutant gas of carbon monoxide (CO). A CO sensitivity of 17.5% is achieved for a gas concentration of 457 ppm at an measurement temperature of 350 C. The response and recovery time of 28 and 64 s, respectively, are obtained. The results ensure that the thermal CVD grown ZnO nanostructured films are applicable for the fabrication of portable gas sensors for atmospheric pollutants.

CHAPTER - 1

GAS SENSORS – AN OVERVIEW

1.1. Introduction

We, the human and all the animals live in an environment where various types of gases and particulate matters are present in the air. Some of them can be toxic or harmful to human bodies if they are present in a huge amount. Also there are chances in industries, laboratories, ships, motors etc., where many types of flammable gases, chemicals are being used in daily basis. Now, sometimes these gases can be ejected or leaked in some areas in such an amount which can generate a major threat to human life, machines and motors. Some of the gases cause skin irritation, breathing problem, some of them remains permanent, some of them can spread to coming generations also. For example, in the month of December, 1984, almost 30 tonnes of toxic methyl isocyanate (MIC) gas was exposed from the Union Carbide factory storage tank in Bhopal [1] causing effective change to the life of almost 6 lakh common people. Thousands of them died and rest of them lived their life with various types of disability like handicapped, blindness, skin disease, lung problem etc. There are so many examples in the whole world, such type of chemical incidents which caused too much harm to human life.

Not only these, if we exclude these types of chemical disaster, toxic gases, flammable gases etc., WHO (world health organization) have published so many reports about air pollution that can also lead to a huge hazard to daily life. And most important output for this air pollution is global warming. The sources that are leading to severe air pollution must be prevented or controlled immediately. Now, we must take a look on the reports that shows a huge number of populations are not only suffering health related problems from the air pollution but it is also causing death [1]. The number of deaths due to pollution from top 10 countries in the world is given in Fig. 1.1. And we can also see that how the death rate has increased from 0.7 million to 1.09 million during 1990 to 2015 in India in Fig.1.2. The air pollution has caused severe effect not only for human but also for animals and birds. So, totally the environment is at a huge risk.

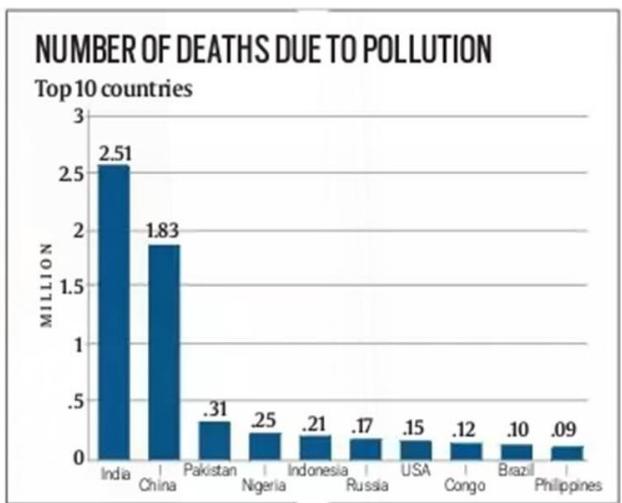


Fig: 1.1. Number of death due to pollution in various countries

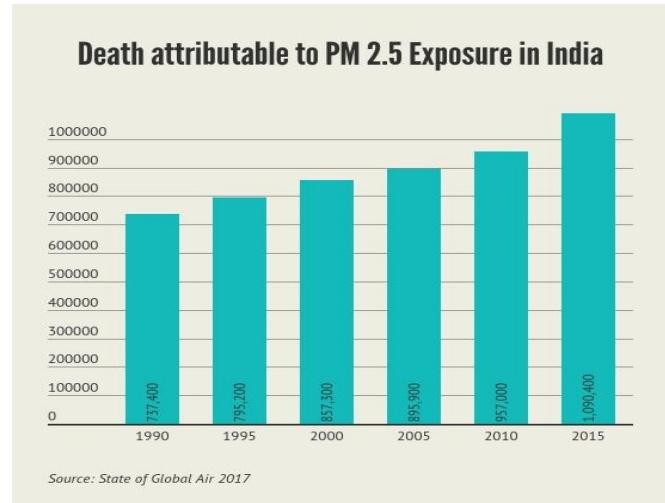


Fig: 1.2. Death due to pollution in India over years

The air pollution can be stopped or necessary steps can be taken to protect the human life if it can be judged or monitored in its initial stage. So, to monitor the chances of these casualties, it is very important to monitor the presence of the gases and to keep it under safe limit by taking necessary steps. For example, when the gas leakage takes place or some polluting gas is increased in amount, a gas sensor should detect it and sound a beep or alarm, so that the surrounding people can easily leave that area or can take the necessary steps to prevent it. Therefore, the usage of gas sensors can avoid disaster due to leakage of gases, by that we can save lives and environment. And, gas sensors are used to monitor the presence of these flammable, toxic and harmful gases and particulate matters in domestic and industrial environment [2].

During the research of p-n junction on semiconductor, it was observed that the junction was also sensitive to many environmental gases. In 1968, Mr. N. Taguchi marketed a simple semiconductor or we can say a solid state gas sensor for the detection of hydrocarbons in LEL combustible range. Though it was not much accurate because it faced several problems like loss of sensitivity with time because of the poisoning and burning out when it was exposed to a high concentration of harmful and toxic gases. Few years later, officially International Sensor Technology of U.S.A introduced a solid-state sensor for the detection of hydrogen sulphide in a range of 0-10 ppm in 1972 [3]. It was the first officially used gas sensor to detect gases present in the environment.

Recent days, gas sensors can actively sense toxic gases like nitrogen oxides (NO_2 & NO), carbon monoxide (CO) and sulphur oxides (SO_x) in the environment when the amount of these gases exceeds a standard limit. And also the gases like ammonia (NH_3), arsine (AsH_3), bromine (Br_2), carbon dioxide (CO_2), chlorine (Cl_2), Chlorine dioxide (ClO_2), Diborane (B_2H_6), halocarbons and refrigerants, Ozone (O_3), Phosphine (PH_3), Silane (SiH_4), etc. can be sensed if the normal environment is amplified by the presence of these gases [4].

Gas sensors can be generally classified into 7 types on the basis of different sensing materials and methods. They are-

1. Capacitance based gas sensors
2. Electrochemical based gas sensors
3. Thermal conductive based gas sensors
4. Optical gas sensors
5. Catalytic gas sensors
6. Acoustic wave based gas sensors
7. Metal oxide semiconductor gas sensors

The various types of properties or parameters have been studied and observed by Korotcenkov [5].

1.1.1. Capacitance based gas sensors

According to its name, it can be easily understandable that the gas sensor works on the mechanism of “changing of capacitance” of the sensor during the presence of the target gas. Now, the capacitance can be varied or it can be changed by changing relative permittivity of the sensor or changing the dielectric constant of the gas sensor.

If we consider humidity gas sensor, high dielectric constant of water at 298 K is 78.5 and while adsorbing it by the gas sensor, relative permittivity will change, so it is a very simple detection mechanism for a gas sensor [6]. Another approach to detect by the gas sensors

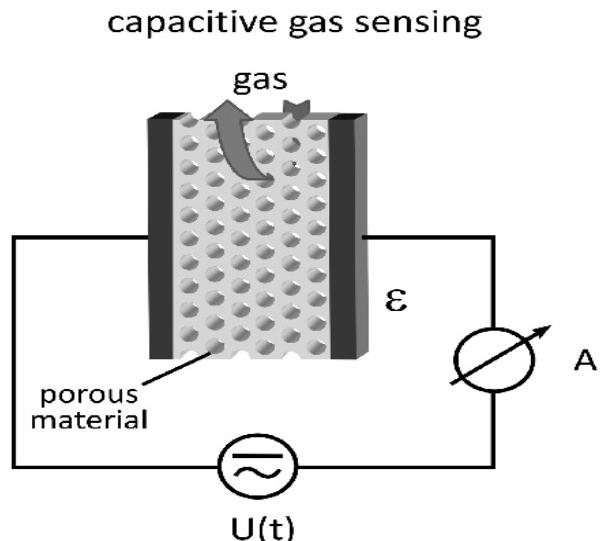


Fig 1.3. Mechanism of capacitive based gas sensor

are based on the changes in dielectric thickness or the distance between the electrodes of the capacitor. The capacitive gas sensors are connected to the inter-computerized electrode arrangement. This arrangement actually used to correlate to the two plates of the capacitor, to measure the difference or variation of the dielectric constant of the capacitor [7]. Now, when the target gas comes in the contact with the film the dielectric constant changes, this is the mechanism of capacitive based gas sensors; now some of the merits and demerits of capacitive based gas sensors are as following-

Merits

Capacitive based gas sensors is very quick responsive with higher sensitivity and also can be operated with small magnitude of external force. Manufacturing cost of the capacitive gas sensors is lower because it has very simple structure [8]. It can sense not only gas but also it can be used to detect non-metallic targets, dense targets and liquids also. It has very well reproducibility and high selectivity so that it can sense the target gas through containers.

Demerits

These types of gas sensors are very sensitive to temperature and humidity etc. so that it can affect a lot if not considered properly. Also, these types of gas sensors actually calculate the capacitance and calculating the capacitance is much more difficult than that of resistance. And if compared to the inductive sensor, the capacitive proximity sensor is not much accurate.

1.1.2. Electrochemical based gas sensor

Electrochemical gas sensors are mainly operated based on the gas concentration inserted into the sensor. For this process, an electric signal is produced by which it can predict the approximate concentration of the target gas [9]. In another way, we can say it acts like a small battery, only the chemical components which are required to produce the electric current are absent in this case. It consists of electrolyte

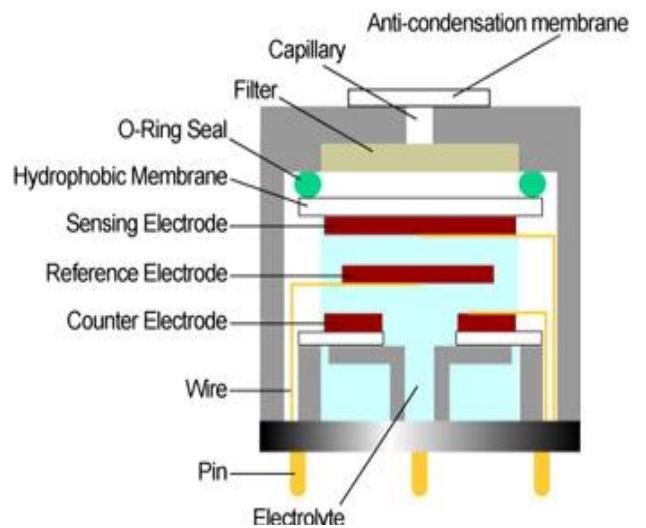


Fig: 1.4. Mechanism of electro-chemical gas sensor

and gels. It also has two terminals, anode and cathode. And, as usual, oxidation takes place at anode and reduction takes place at cathode. Firstly, target gas comes to contact with the sensor, then it passes through a membrane within it. Then, it comes to the contact with the electrolyte where an electrochemical reaction takes place. Now, either it takes place at anode or cathode as described earlier. During the oxidation reaction which takes place at anode creates or forms the current flow from the working electrode to the conductor electrode through an external circuit. And if reduction reaction takes place, it results to form the current flow in the opposite direction [10]. Now, the magnitude of this current flow directly depends (proportional) to the amount of gas present at that instant. Thus, the magnitude is measured by some external unit. And this way the concentration of the target gas also can be determined. If the variation of electric current flow can be measured or verified, then the differences in target gas also can be determined.

Merits

Electrochemical sensors are very sensitive to the gases and that's why it can sense a long range of gases and it can also sense various concentrations of the gases. It can detect different gases in different concentration even in ppm range. It does not require any higher power requirements but can give a simple, linear and good resolution [11]. Though it can give a simple and linear resolution, once it is calibrated to a known concentration it can give also very exact data or reading for a particular gas. And most importantly, this type of sensors does not get poisoned by other gases [12]. It can detect various gases repeatedly but remains accurate and fresh when it is used for a different target gas.

Demerits

Most common but most important demerits of an electrochemical sensor is high temperature. High temperature and low humidity can cause the electrolyte to dry out. Also, the temperature variation during the sensing can differ the output data of the sensor. So, it is very important to keep the temperature constant or as stable as possible [11]. Also the variation of gases can cause shorten of life which is usually extends up to six months or one year. Electrochemical sensor can sense various types of gases at a time, if it is an advantage but sometimes interference from other gases can be caused which can lead to false output data.

1.1.3. Thermal conductive based gas sensor

This type of gas sensors detect the gases based on their thermal conductivity. The sensor calculates the thermal conductivity with respect to a reference gas such as air and gives the output data of percentage volume ranging 0 to 100% [13]. And this can be changed by varying the temperature of the target gas. A compensator bead which is in a sealed enclosure of air is used as reference while calculating the thermal conductivity of the target gas. Now, the sensor bead and reference bead are connected in a Wheatstone bridge and supplied with a constant voltage. When the detector bead comes in contact of the target gas a rise or drop in bead temperature occurs. This temperature difference results in the formation of resistance. Finally, the difference in temperature also results the difference in thermal conductivity of the target gas with respect to that of the reference gas [14]. This method is continuous and accurate if compared with the chemical processes of sensing. But, it is costlier than the other type of sensing equipment. These thermal conductive based gas sensors can sense more than one gas at a time if the thermal conductivity of the target gases is different [15].

Finally, we can conclude that this type of gas sensors are effective and also can be used because it does not pollute the environment and does not require oxygen for comparison and high power supply.

Merits

Most important, it can sense more than one gas at a time, without changing any other conditions like temperature, power supply etc. It has robust and simple structure which is actually a Wheatstone bridge construction. It has a wide measurement range as it measures and gives output data with respect to a referencing gas. And it can be operated easily in absence of oxygen [12].

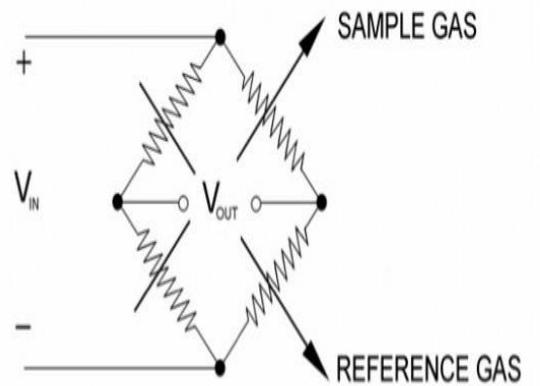


Fig: 1.5. Mechanism of thermal conductive gas sensor

Demerits

This type of gas sensors is bit costlier than the other types of gas sensors. It also needs a constant voltage supply may be it is small but it can be interrupted because of the interruption of power source. So, then it can misbehave during the measurement. Also, while sensing the gases, the difference in the resistances causes the formation of heat that's why sometimes the measurement can be disturbed because the percentage volume can change while varying the temperature. So, it is very much necessary to maintain the temperature of the wire connected through the Wheatstone bridge.

1.1.4. Optical gas sensors

Gas sensing by optical method is much simpler and straightforward. It can achieve higher sensitivity, selectivity and stability than non-optical methods with much longer lifetime than the other types of gas sensor. The optical gas sensor mainly depends on the working principle of spectroscopy [16]. And the spectroscopy analysis mainly based on the techniques like adsorption and emission spectrometry. Besides this, there are also many types of optical sensors available in the research field. They are differential optical absorption spectroscopy (DOAS), Tunable diode layer absorption spectroscopy (TDLAS), Raman light detection and ranging (LIDAL), differential absorption LIDAR (dial), intra-cavity absorption spectrometry (ICAS) etc. [17]. Intra-red source gas sensors based on optical sensing principle is also very important and it is so much accurate that it is being widely used for better sensing [16]. All of these previously discussed gas sensors are very accurate and gives an exact result. But the gas sensors are costly because more accurate instrument costs more to manufacture or maintain. And finally as the gas sensors are optically visible so, gas detection process also very easier than the others.

Merits

Optical gas sensors are much accurate and can give exact data even if the temperature varies or any other environmental changes occur. It can detect the changes even if in Nano scale. It can also work in absence of oxygen and also very easy to operate. It can't be affected by the electromagnetic interference and can be used in a wider range. By this type of gas sensors, the detection of target gases can be experienced visually. So, optical gas sensors can be used in various areas to detect the target gases properly.

Demerits

The main demerit of the optical gas sensor is the result due to the ambient light interference [13]. Because the spectroscopy and emission properties can be changed for a target gas due to the presence of ambient light. Also, the manufacturing cost and maintenance cost is very high as it has is very sensitive, small and costly items in the sensors. So, the optical sensors must have the light resistive arrangement for perfect analysis of gas detection.

1.1.5. Catalytic gas sensors

This type of gas sensors actually consists of small detecting elements “pellets” of crystal loaded ceramic which can vary resistance in presence of various target gases. So, these types of sensors are called ad “pellistors” which is a combination of “pellets” and “resistor”. Now, one type of pellistors is catalytic gas sensors. It particularly calculates or measures the heat produced by the molecular recognition reaction on the sensors [18]. That means when the target gases come to the contact with the sensor, the gases get burned and for that the temperature increase or decreases. As in the sensor, exothermic or endothermic reaction occurs for this process. Catalytic sensors consist of a platinum coil which is used as a heater. Now, this coil is heated and the combustible gas will burn on the surface of catalytic layer. For this, the difference in temperature also occurs. This change in temperature generates resistance change in the system. So, by calculating this resistance change we can measure the concentration of the target gas also [17]. Catalytic gas sensor gets the actual data by burning the target gas; so we can say that continues oxygen flow is too much necessary for the burning. Catalytic gas sensors can also get proper output sensitivity even at lower temperatures.

Merits

The merit of catalytic gas sensor are first of all it is very simple and manufacturing cost of this gas sensor is very low. It can sense in low temperature and even when other gases are there in that area. Because, it is measured only when the target gas is being burned. So, the measurement is also safe and it can give an exact data. Also after measuring it becomes much more stable and it can be improved.

Demerits

Continuous flow of oxygen is needed for throughout the process of burning. Another demerit of this type of gas sensors is that it can be poisoned by lead, chlorine, silicon etc. Now, for this poisonous character, the actual data also gets disturbed. Sometimes, the wire in the gas sensors gets heated so much that the heat measurement coil can break if the temperature goes very high.

1.1.6. Surface acoustic wave based gas sensor

Surface acoustic wave based gas sensor can be termed as sound oriented gas sensors, which travels through a surface of elastic material. For this, the amplitude of the sound waves starts to decay with their displacement into the material. These types of gas sensors use a sensor with piezoelectric materials like gallium arsenide or quartz crystal [19]. This can be generated by applying an oscillating signal designed for the surface. The surface transducer forms like a comb shaped interdigitated electrodes of many pairs. Now, the piezoelectric material vibrates in a resonance frequency of more than 600 MHz, which is a huge amount of surface energy. Lord Raleigh first explained that the properties of propagation of waves along the plane surface of elastic solid, this role is played by the SAW transducer. Now, the electrical signal at resonant frequency excites the sound wave which is passed through the transducer to calculate the change in velocity, surface temperature, viscosity and mass loading etc. [20]. For example, if the acoustic wave velocity is reduced, a frequency shift is observed. Now, this change in the transducer helps to detect the mass of the contaminant deposited which is actually the detecting target gas, for gas sensors. This is how, a surface acoustic wave gas sensor works.

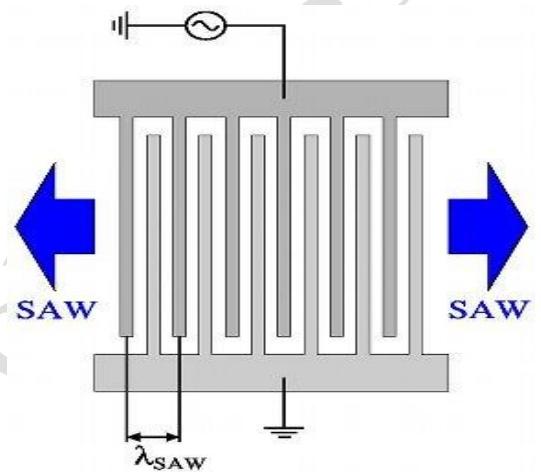


Fig: 1.6. Mechanism of SAW gas sensor

Merits

It can sense nerve and blister agents. Though it needs an electric signal but it is battery less so can get a continuous power supply. It is normally used for wireless applications. It can be also placed in

rough, harsh and rotating plates [12]. It has a longer lifetime than the other types of gas sensors. It does not spread any other secondary pollution.

Demerits

It has low sensitivity that means to sense properly the amount of target element is required more compared to other processes of sensing. Other environmental condition like temperature, humidity, sound etc. can affect the output data. So, it is very sensitive to environmental change. Finally, it has very smaller size and very sophisticated structure. So it is very hard to handle [12]. Otherwise the total system can be disturbed and that causes high differences in output data.

1.2. Metal oxide semiconductor gas sensors

Considering the influence factors on gas sensing properties of metal oxides, it is necessary to discuss the sensing mechanism of metal oxide gas sensor. The exact fundamental mechanisms of gas sensing are still controversial, but essentially trapping of electrons at adsorbed molecules and band gap reduced by these charged molecules are responsible for a change in conductivity [21].

So, to understand this mechanism based on conductivity we should discuss about the band theory. Band theory states that within a lattice there exists a valence band and a conduction band. The separation between these two bands is a function of energy, particularly the Fermi level, defined as the highest available electron energy levels at a specific temperature. There are three main classes of material in band theory, they are- Insulator, Conductor and Semi-Conductor. Insulators have a large gap between the valence and conduction band as such a lot of energy is required to promote the electron in to the conduction band and so electronic conduction does not occur. Conductors have the Fermi level lying within the conduction band. Semiconductors have a sufficiently large energy gap so that at energies below the Fermi level, conduction is not observed but above the Fermi level, electrons can begin to occupy the conduction band, resulting in an increase in conductivity [22].

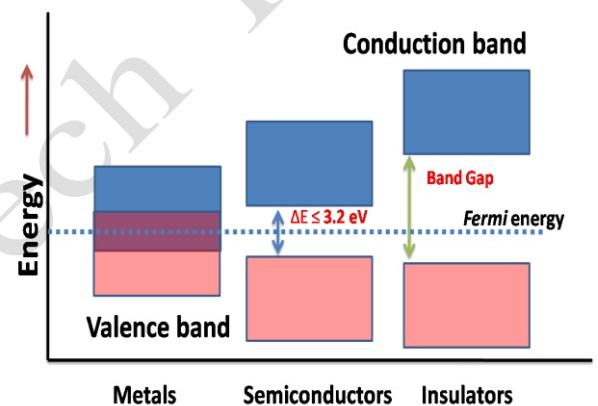


Fig: 1.7. Band gap

Now, it is also important to know why only semiconductors are used and how these semiconductors are used as gas sensors generally. When the target gas comes in the contact with the surface of the metal oxide film it results in a change in charge carrier concentration of the material. This change in charge carrier concentration also changes the conductivity or resistivity of the material [23]. So, the change in carrier concentration of the material, i.e. conductivity of the material only occurs for semiconductors.

There are 2 types of semiconductors, n-type and p-type. An n-type has electrons as majority charge carriers, and while interacting with a reducing gas an increase in conductivity occurs. Conversely, an oxidising gas plays role to deplete the sensing layer of charge carrying electrons which results a decrease in conductivity. A p-type semiconductor is a material which conducts positive holes being the majority charge carriers; hence, the opposite effects are observed with the material and showing an increase in conductivity in the presence of an oxidising gas. A resistance increase is also observed with a reducing gas, where the negative charge introduced into the material reduces the positive (hole) charge carrier concentration [24]. For example, O₂ molecules are adsorbed on the surface of metal oxides, and then they would extract electrons from the conduction band and trap the electrons at the surface in the form of ions. Reaction of these oxygen molecules with reducing gases or a continuous adsorption and replacement of the adsorbed oxygen by other molecules decreases and can reverse the band energy, causing an increase in conductivity [25].

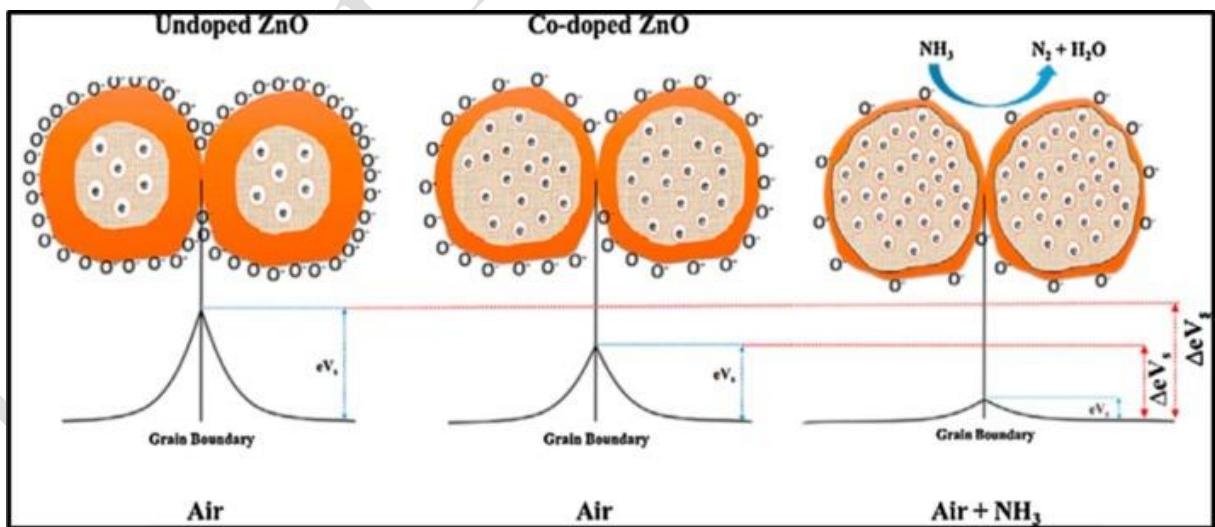


Fig: 1.8. Sensing mechanism of ZnO grown thin films

Metal oxide sensors are commonly called as chemiresistors. The MOS gas-sensing materials are typically n-type or p-type semiconductors under normal atmospheric conditions and it has a typical working temperature of 300–600° C to develop an electron-depleted surface layer [26]. The presence of gases in the surrounding atmosphere that reacts with the reactive oxygen species at the MOS surface measures the depletion layer thickness, and this gives us the idea to the measurable changes in the resistance of the material. Gas molecules interacting with the metal oxides either act as a donor or acceptor of charge carriers (Receptor function), and alters the resistivity of the metal oxide (Transduction function). The increase or decrease of resistance of the metal oxide thin film depends upon the type of majority carriers in the semiconducting film and the nature of gas molecules (whether oxidizing or reducing) in an ambient atmosphere. For n-type materials, oxidizing gases (acceptor) increase the resistance of thin film while, reducing gases (donor) decrease and are correspondingly converse for p-type materials.

For example, reducing gases like CO and H₂ react with the highly sensitive MOS surface and remove some of the absorbed oxygen while injecting electrons back into the MOS, and this causes a reduction in the thickness of the depletion layer. On the other hand, oxidizing gases such as NO₂, collects even more electrons from the solid, thereby increasing the thickness of the depletion region shown in figure 1.8 [27].

So, these are the advantageous qualities for choosing the semiconductor metal oxides. Since 1962 it has been known that absorption or desorption of a gas on the surface of a metal oxide changes the conductivity of the material also changes in the depletion layer, this phenomenon was first demonstrated by using zinc oxide thin film layers [28].

The sensitivity of a surface to a target gas can be as low as parts per billion (ppb). It is highly desirable that metal oxide semiconductor sensors have a large surface area, so it has the ability to adsorb as much of the target analyse as possible on the surface that gives a stronger and more measurable response even at low concentrations.

Advancement in

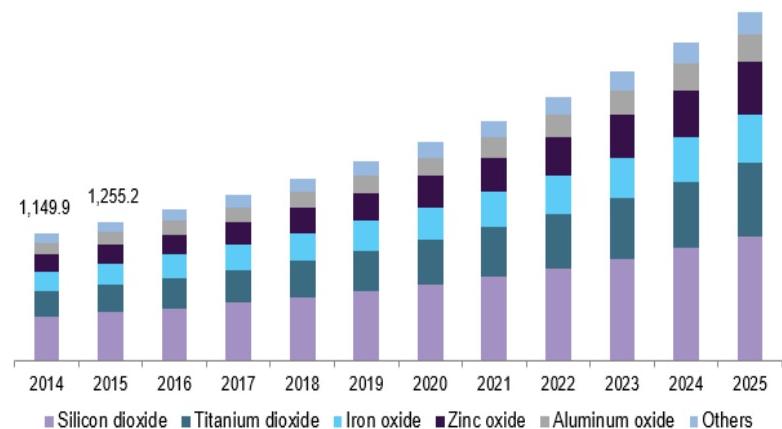


Fig: 1.9. Usage of ZnO for nanomaterial structure

fabrication methods have also given the opportunity to enable the production of low-cost sensors with improved sensitivity and reliability compared to those formed using previous methods [29]. Production costs are low due to the simplicity of manufacturing of metal oxide semiconductor sensor devices. Their ability to be produced quickly and on a large scale with easily controllable processes makes them the most desirable way to process the sensing of gas sensors. Metal oxide semiconductor gas sensors are utilised in various ways of different roles and industries. They are relatively less expensive compared to other sensing technologies, robust, lightweight, long lasting and benefit from high material sensitivity and quick response times. They have been also used extensively to measure and monitor the trace amounts of environmentally important gases such as carbon monoxide.

Carbon monoxide (CO) sensing is important because CO is a colourless gas, with no odour or taste, making it undetectable to humans. CO is constantly in the air in a large amount from a faulty gas powered boilers that lead to annual deaths. CO concentrations are particularly high in areas of industry, where fossil fuels are combusted for energy purposes, and in cities where there are high levels of traffic. Carbon monoxide causes dizziness, confusion, breathing problem and many more physical problems; the occupant may be in no condition to readily observe this change [30].

1.2.1. Zinc Oxide

Nanostructure materials drew the attention of scientific research field due to their interesting physical and chemical properties, and potential and versatile applications. Compared to the other nanostructure metal oxides, zinc oxide (ZnO) is the most studied material and still continues to maintain the research interest because ZnO belongs to a group of II-VI semiconductor which acquires a vast band gap equal to 3.37 eV, also it has extensive exciton binding energy of 60 meV at room atmospheric condition, and good electrical, optical and piezoelectric behaviours [31]. ZnO thin films also have been broadly researched due to their low cost, non-toxic nature, magnificent electronics, and easy

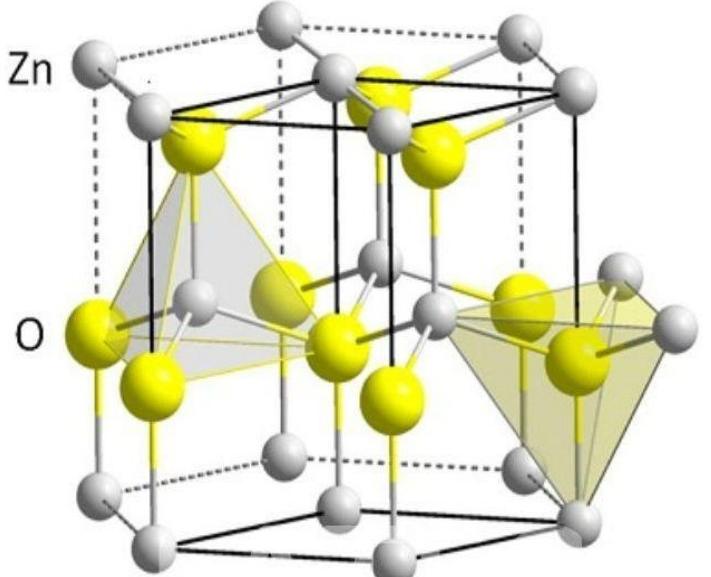


Fig: 1.10. Hexagonal structure of ZnO Wurtzite phase

fabrication properties. The other characteristics for which ZnO is selected as a sensing material are crystallinity, specified orientation, crystallite size, micro-strain, dislocation density, texture coefficient and morphology [32]. And the crystalline hexagonal Wurtzite structure has been shown in Figure 1.10.

The chemical and physical properties of ZnO can be modified when changes occurred into the procedure of its synthesis. ZnO has various potential applications in various fields and important multifunctional material with applications like short-wavelength light-emitting diodes and ultraviolet lasing diodes, solar cells, UV-absorbers, transparent conductors, transparent electrodes, field emission displays, transducers, catalysts and gas sensors etc. Recently, ZnO spherical structures have gained more research attention due to their expected applications in Nano-lasers, photo catalysis, energy storage and conversion, data storage and memory, and advanced optoelectronic and piezoelectric devices [33].

Table:1.1. Physical properties of ZnO

Molecular Formula	ZnO
Lattice Constants	a=b= 3.253 nm & c=5.201 nm
Density	5.6 gm/cm ³
Melting point	2248 K
Energy Gap	3.08 eV, direct
Intrinsic Carrier Concentration	< 10 ⁶ cm ⁻³
Excitation Binding Energy	60 meV
Electron Effective Mass	0.24

ZnO has been extensively used as a gas sensing material because it has high mobility of conduction electrons and good chemical and thermal stability under the operating conditions of sensors. ZnO as gas sensors will give a better result when the material is processed in a controlled size in nanometres. It is well-known that the sensing mechanism of ZnO belongs to the surface-controlled type, in which the grain size, defects, and oxygen-adsorption quantities play important roles in sensing

response [34]. In several recent reports, ZnO nanostructures have been demonstrated that it has good sensitivity and sensitivity and the response time of ZnO based sensors strongly depend on the size, specific surface area, and morphology of the processed structure. The ZnO thin films is verified to be a suitable material for sensing various toxic and unsafe gases like NH₃, NO_x, CH₄, H₂, CO, H₂S etc. [35]. Therefore, investigations and correlative mechanism studies of highly oriented, aligned and ordered arrays of ZnO nanostructures are of critical importance for the development of the novel devices. For the growth of 1D ZnO nanostructures, there are a number of methods present, for example thermal CVD, Hot wire CVD, hydrothermal process, and thermal Evaporation. Among all deposition processes, the thermal CVD of Zn powder is a simple and effective method for growing uniform and aligned ZnO nanostructures. Most ZnO research has been focused on the preparation of one dimensional nanostructure. It has been observed that the properties of ZnO nanomaterials strongly depend on their dimensions and morphologies.

1.3. Aim of this work

- Synthesize of ZnO nanostructured thin films by thermal CVD technique.
- Characterization of the physical properties of prepared ZnO nanostructures.
- Study on the gas sensing characteristics of prepared ZnO nanostructures.

CHAPTER - 2

THERMAL CHEMICAL VAPOUR DEPOSITION OF ZnO

2.1. Introduction

A thin film is a layer of material, which have a length of range from fractions of a nanometre to some several micrometres in thickness. And, the controlled synthesis of materials, normally known as deposition of thin film is a fundamental step to use it in many applications [36]. Thin film deposition is the technology of applying a very thin film of material or the thickness of a few atoms onto a “substrate” surface which has to be coated, or onto a previously deposited coating to form layers. Thin film deposition processes are the main technology of today’s semiconductor industry, solar panels, CDs, disk drives, and optical devices industries [37].

Thin films can be prepared through main two methods: Physical vapour deposition (PVD) and Chemical vapour deposition (CVD).

PVD refers to that range of technologies where a material is released from a source by heating and vaporizing the material and then deposited on a substrate using mechanical, electromechanical or thermodynamic processes. This deposition does not contain any chemical reactions or any chemical changes. PVD can be differentiated by following parts-

- Thermal Evaporation
- E-Beam Evaporation
- Pulsed Laser Deposition
- Ion-plating Evaporation
- DC Sputtering
- RF Sputtering
- Magnetron Sputtering
- Molecular Beam Epitaxy (MBE)

CVD occurs when a volatile fluid material face a chemical change on a surface leaving a chemically deposited coating. CVD is used to produce highest-purity, highest-performance solid materials in the

form of thin film or nanostructures. This type of deposition occurs with a change in chemical properties and chemical nature of the film. So, by these vapour deposition techniques, we can estimate a different type of products synthesized within it.

Some of the important CVD techniques are-

- Thermal CVD
- Metal organic chemical vapour deposition (MOCVD)
- Plasma Enhanced Chemical Vapour Deposition (PECVD)
- Sol-gel method
- Spray Pyrolysis
- Electroplating
- Atomic Layer Deposition (ALD) [38]

Among the described processes, thermal CVD has been employed in the current study for material synthesis because it is a very simple and easier process than the others; the gases can be reacted with other gases or decompose to produce stable reaction products and deposit on the substrate at any temperature, and without creating vacuum. It is also less costly to synthesis thin films. It has wide range of chemical reactions, reactants, and applications to deposit on the substrate. Different types (crystallinity) of thin films like poly-crystalline, Single-crystalline and amorphous can be processed by this single technique. Also, semiconductors (IV, III-V, and II-VI), metals, dielectric and superconductor thin films can be synthesized by this process [39]. Thus, it is the most versatile deposition technique. As we have deposited ZnO by thermal CVD, the technique is described in detail below.

2.2. Thermal CVD

CVD is a chemical process in which gaseous precursors are used for synthesis. Precursor gases are moved into a chamber with the substrate being placed over a glass or quartz tube [40]. And then along with the gas passing through the tube, the temperature is also increased in a controlled manner. Gases must be in a streamline continuous flow that can be controlled by a mass flow controller. And the temperature also can be controlled by the control box or temperature controller. The temperature is increased to a designated value which should be higher than the melting point of the material. So, after reaching the temperature the material starts vaporizing and then reacts with the gases passed through the

system. And the product which is produced after the reaction starts to deposit on the substrates. Figure 2.1 shows the schematic diagram of a typical thermal CVD system.

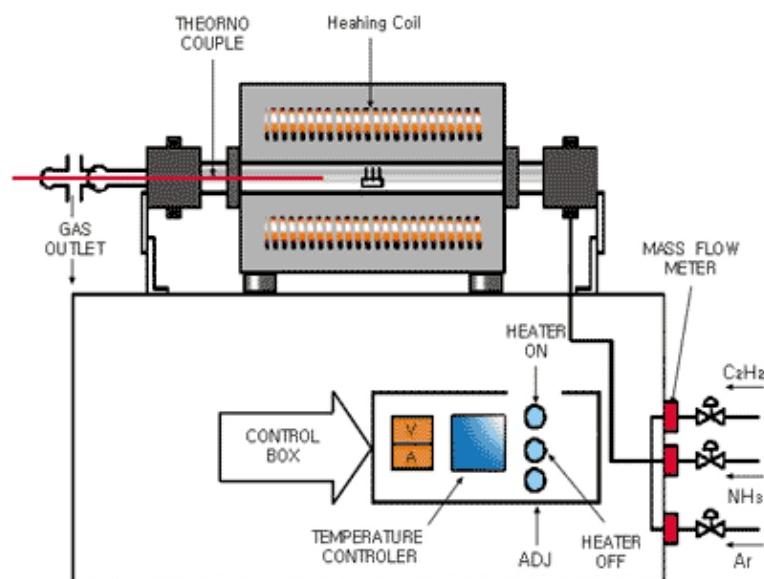


Fig: 2.1. Schematic diagram of Thermal CVD system

Thermal CVD has several components which are important to carry out the deposition process properly. They are- mass flow controller (MFC), furnace, PID temperature controller, heating rods, gas cylinders, quartz tube.

2.2.1. Mass flow controller

A mass flow controller is a type of gas flow controller which is independent of conditions or changes in pressure that controls the flow rate of gases according to a set flow rate through an electric signal. Mass flow controllers have a flow rate measurement section which includes a sensor, bypass, flow rate control valve and special circuitry [41]. The gas is injected from an inlet joint, and then it is divided so that it flows over the flow rate sensor as well as the bypass also. The sensor measures the mass flow rate of the gas, and then flow rate control valve make corrections of the flow rate so that the difference between the measured flow rate and the flow rate received from the external flow rate setting signal becomes 0 (zero). This process forms a loop circuit, so if any changes in gas pressure take place, the flow rate should not be changed and it will instantaneously be corrected, so that the flow rate can be stable.

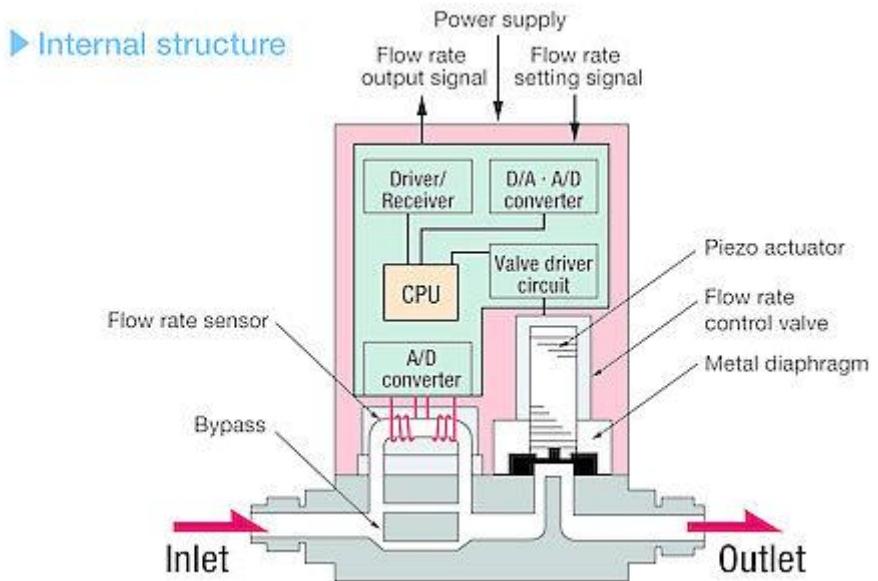


Fig: 2.2. Working principle of a mass flow controller

2.2.2. PID temperature controller

PID temperature control is a loop control feature found on most process controllers to improve the accuracy of the process now a day. Here PID stands for proportional, integral, and derivative. Each of these elements can relate to the variance in the process of temperature versus the set point temperature in a period of time [42]. PID temperature controllers work using a formula to calculate the difference between the desired set point temperature and current process temperature, then predicts how much power to be used in the process to ensure the increasing or decreasing temperature remains as close to the set temperature as possible by eliminating the impact of process of environmental changes. The temperature controller takes an input from a temperature sensor and has an output which is connected to a heater or a fan to increase or decrease the temperature. If the PID temperature controller is tuned properly, then it will compensate for the disturbance and bring the process temperature back to the set point temperature,

but also reduce power as temperature approaches to the set point temperature so that it doesn't overshoot and risk as damaging the product with too much heat [43]. By this PID controller, required temperature can be set, ramp rate can be adjusted, and also deposition time can be adjusted. It can be controlled manually also.

2.2.3. Furnace & heating rods

Furnace and heating rods can be described at a time because both are dependent on each other's. Furnace is that part in CVD where the boat and the substrates are placed for deposition and then gases are passed so that the reaction takes place and finally deposition occurs. In this furnace an alumina tube is surrounded by 4 heating rods, which are being heated by resistive heating. When the temperature is set by the PID controller then the rod starts heating the tube. It can be observed that around 400°-500°C, the rods become red hot. And the furnace should be closed in such a way that the heat should not come out or the heat loss must be minimum.

2.2.4. Gas cylinders

Gas cylinders contain required gas for the reaction, which are passed through the tube. Gas cylinders also have some colour by which it can be verified that which gas is inside that cylinder. For example, oxygen is filled inside a black cylinder. Also, some pressure controller can be fixed in the outlet of the cylinder to know the cylinder and outlet pressures. The outlet pressure can be fixed for the process as required by the MFC, and a continuous flow can be delivered through the tube.

2.2.5. Quartz reactor

Quartz reactor is very essential for the CVD process. In CVD technique the temperature can be increased up to 1000 °C; it depends on the melting point of the materials which is being the target e.g. Zn powder. Hence, if the process temperature is high, the reactor must be made of such material which has a higher melting point. That's why Quartz is used as the reactor material. Also, the transparency of quartz makes the loading and unloading of precursor/substrate assembly easier.

2.3. Thermal CVD of ZnO

In this project, ZnO has been deposited on the substrates like alumina, sapphire, silicon, and nickel to use it as a semi-conductor metal oxide solid state gas sensor. First of all, small pieces of all the

substrates were collected by cutting the wafers. And then the pieces were cleaned by Ultrasonic heater. 2/3rd of the Ultrasonic heater was filled by distilled water. Then, the temperature was set around 50 °C. After reaching the temperature, the substrates were dipped within TCE and then acetone. For each part, the substrates were kept for 10 minutes in the heater. After cleaning in TCE and Acetone, substrates were taken out and Nitrogen gas was used to dry the rest of acetone droplets remained on the substrates. And, the substrates were kept in a desiccator, so that they can't be contaminated easily.

Pure Zn powder of approximately 0.3 g. was taken for the synthesis. Zn power was kept in the bottom surface of a ceramic boat in such a way that the distribution of Zn must be uniform throughout the boat. The ceramic boat which was used in this process had a length of 100 mm, height of 10 mm and width of 15 mm. After loading the Zn powder, each type of the substrates was placed over the ceramic boat like a bridge connecting between the 2 sides of the boat.



Fig: 2.3. Picture of the ceramic boat

Now, the ceramic boat was loaded inside the quartz reactor very carefully and placed at the centre of the furnace. After placing the boat, end coupling was carefully set at the both sides of the quartz tube; one side was connected to the mass flow controller for gas inlet and the other side was connected with the outlet so that the gases can flow outside after reaction. In this case, 2 types of gases were used for the deposition, one of them was an inert gas, and the other one was reaction gas, i.e., oxygen to oxidize the Zn metal. Depending on availability, argon or nitrogen was used as the inert gas.

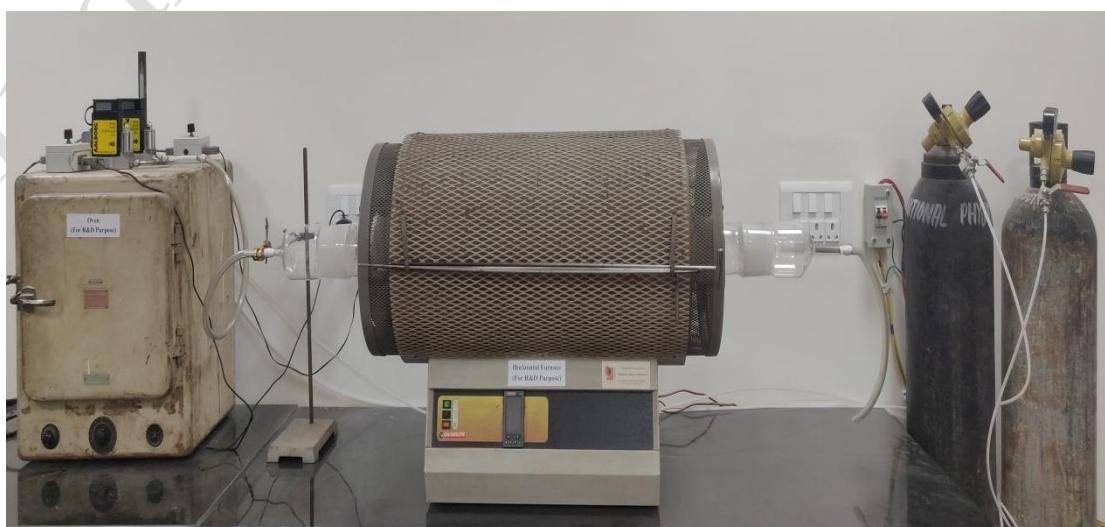


Fig: 2.4. Thermal CVD experimental set up

Now, the Argon gas was allowed to flow into the reactor through the MFC at controlled flow rate of 2.5 LPM (litre per minute). The MFC had a range of 0-5 LPM for Argon gas flow, and was made by MKS. This process continued for 15 minutes so that the ambient gas in the reactor was flushed out and the whole reactor was filled with argon. The chances of contamination of material synthesis were reduced by this process. After 15 minutes, the temperature was increased at a ramp rate of 25 °C/minute by the PID temperature controller. The PID controller was manufactured by Carbolite. This process was continued until the temperature was raised up to the designated temperature. The ZnO synthesis was carried out at various temperatures such as 600, 650 and 700 °C. The tube became red hot due to the high temperature. After reaching the deposition temperature, oxygen gas was opened and the flow rate of oxygen was set at 50 sccm (standard cubic centimetre per minute) using another MCF. Simultaneously, the flow rate of argon gas was reduced to half i.e. 1.25 LPM. The MFC for oxygen gas had a range of 0-50 sccm and was made by MKS. After passing the 2 gases, the deposition process was initiated, and took place for 15 minutes. After 15 minutes, the temperature was set to room temperature and the heater was shut down. As there was have no cooling system, the furnace was allowed to cool in the normal environmental condition. When the temperature was dropped to approximately around 400°C, oxygen supply was interrupted or closed, and the furnace was cooled to the room temperature only under the inert gas flow. The supply of insert gas was closed at the end. When the whole furnace and tube was cooled down the boat assembly was taken outside and the substrates were collected very carefully and stored in a vacuum desiccator for their characterization.

CHAPTER - 3

CHARACTERIZATION TECHNIQUES

3.1. Introduction

Nanostructured semiconductor materials can be synthesized by various physical and chemical processes. The processed material also can differ depending on the precursor materials, like it can be ZnO, or it can be SnO or it can be some other material. Nanostructured materials cannot be characterized by naked eyes. So, there are many characterization techniques like XRD, SEM, PL etc. which help to characterize the processed materials [44]. Now, characterization is required because we need to know the actual elements present after the synthesis of the nanostructured semiconductor. We can also study if there are any contaminations in the processed materials, percentage of various elements present in the nanostructured materials, morphology of nanostructures etc. An important issue is the correct interpretation of the experimental results obtained by characterization tools. To confirm this, in this chapter, we will describe the techniques employed for the current study to characterize the physicochemical properties of ZnO nanostructures. This chapter represents the various characterization techniques used in the present work and it also includes the basic principles of the characterization techniques in brief.

- X-Ray diffraction technique (XRD)
- Field emission scanning electron microscopy (FESEM)
- Energy dispersive X-Ray analysis (EDAX)
- Photo-luminescence
- Raman Spectroscopy

3.2. X-Ray diffraction (XRD)

The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another after they leave the crystal surface. The phenomenon is called X-ray diffraction. This process is followed by the Bragg's law, which was invented by English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913. The formula derived by them-

$$n\lambda = 2d \sin \theta$$

They stated that different faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, θ). The variable ‘d’ is the distance between atomic layers in a crystal, and the variable lambda ‘ λ ’ is the wavelength of the incident X-ray beam [45]. Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures.

Now, for these characteristics of XRD helps to detect or Measure the average spacing between layers or rows of atoms. It also helps to determine the orientation of a single crystal or grain. It can be used to find the crystal structure of an unknown material. And it can also Measure the size, shape and internal stress of small crystalline regions. So, we can estimate that the synthesized material is either poly crystalline or single crystalline or amorphous. And we can also determine the particular materials present within it. Because when we get the XRD data, it contains some peaks for different planes. According to JCPDS data, the peaks correspond to a particular angle for a particular material. So we can easily determine if there are other materials or not.

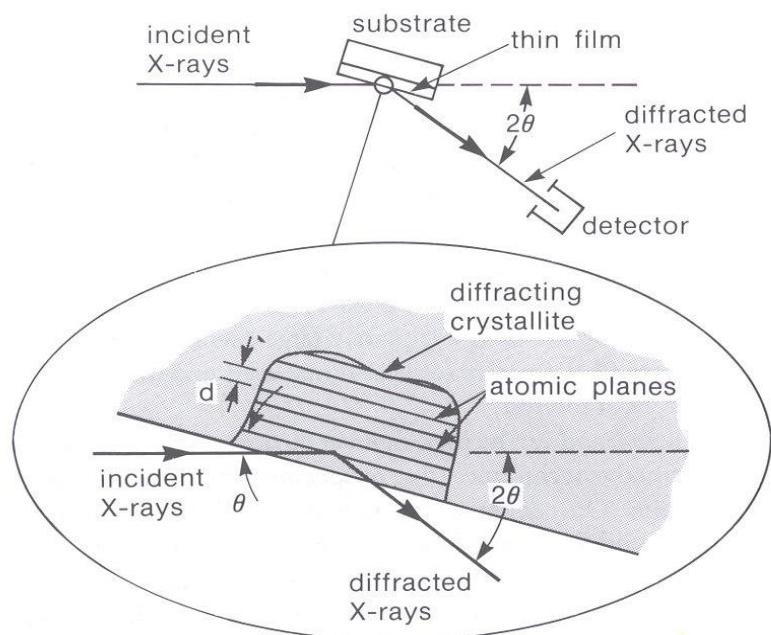


Figure 3.1. Working principle of X-ray diffraction

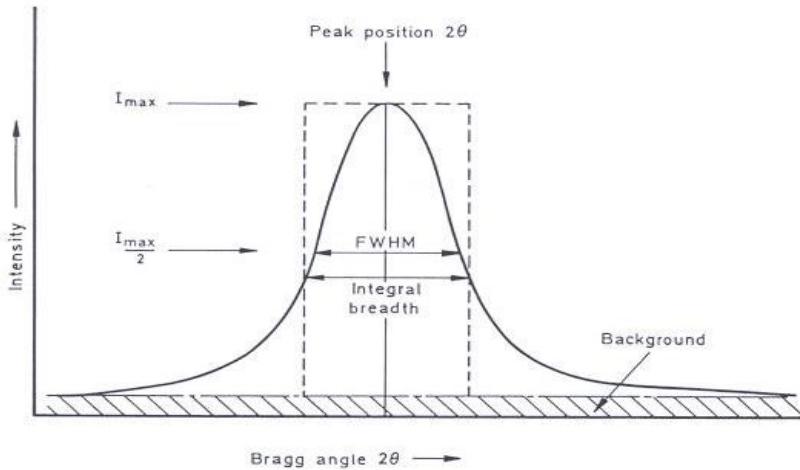


Figure 3.2. Schematic representation of full width at half maximum (FWHM)

This is the block diagram of XRD; this is how we finally get the diffraction data. Also we can get the d-spacing, lattice parameters, peak position, peak width and peak intensity.

d-spacing is calculated from $\lambda = 2d_{hkl} \sin\theta_{hkl}$

$$d_{hkl} = 1.54\text{\AA}/2\sin\theta_{hkl}$$

where, $\lambda = 1.54\text{\AA}$ (Cu $\kappa\alpha$); standard JCPDS data. Now, $d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$;

$$\text{For a simple cube, } a=b=c=a_0, \quad a_0 = d_{hkl} \sqrt{h^2 + k^2 + l^2}$$

And, we can also measure the peak width, full width at half maximum (FWHM) [46].

From the above figure we can also get the parameter based on their length equality or inequality and their orientation (the angles between them, α , β and γ) a total of 7 crystal systems can be defined. For example, for hexagonal structure the values are, $a=b\neq c$ & $\alpha=\beta=90^\circ$, $\gamma=120^\circ$.

Finally, we can say XRD helps to characterize the elements so that we can find the crystalline structure, lattice parameters, peak values etc. so that we can get the primary ideas about the synthesized film. XRD is a non-destructive technique that's why the processed film doesn't get disturbed and it can be again used for further characterization of that film [47].



Figure 3.3. X-ray Diffractometer at CSIR-NPL.

3.3. Field emission scanning electron microscopy (FESEM)

FESEM instrument plays an important role in the field Nano-technology, though we can see the macroscopic objects from our naked eye using light, but if we want to analyse the surface morphology at atomic level or at nanostructure level it requires electron microscope. The electron column of the SEM consists of an electron gun and two or more electromagnetic lenses operating in vacuum. The ability for a SEM to provide a controlled electron beam requires the electronic column be under vacuum at a pressure of at least 5×10^{-5} Torr. The electron gun generates free electrons and accelerates these electrons to energies in the range of 1-40 keV in the SEM [48]. The purpose of the electron lenses is to create a small, focused electron probe on the specimen. Most SEM's can generate an electron beam at the specimen surface with spot size less than 10 nm in diameter while still carrying sufficient current to form acceptable image.

In order to produce images the electron beam is focused into a fine probe, which is scanned across the surface of the specimen with the help of scanning coils can be seen in the above figure. Each point on the specimen that is struck by the accelerated electrons emits signal in the form of electromagnetic radiation. Selected portions of this radiation, usually secondary (SE) and/or backscattered electrons (BSE), are collected by a detector and the resulting signal is amplified and displayed on a TV screen or

computer monitor [49]. The resulting image is generally straight forward to interpret for topographic imaging of objects at low magnifications.

By the SEM, we can see the morphological structure of the element. It can be nanorods or nanotubes or many more nanostructures etc. This can be only seen by the electron microscope. That's why SEM is important for the characterization

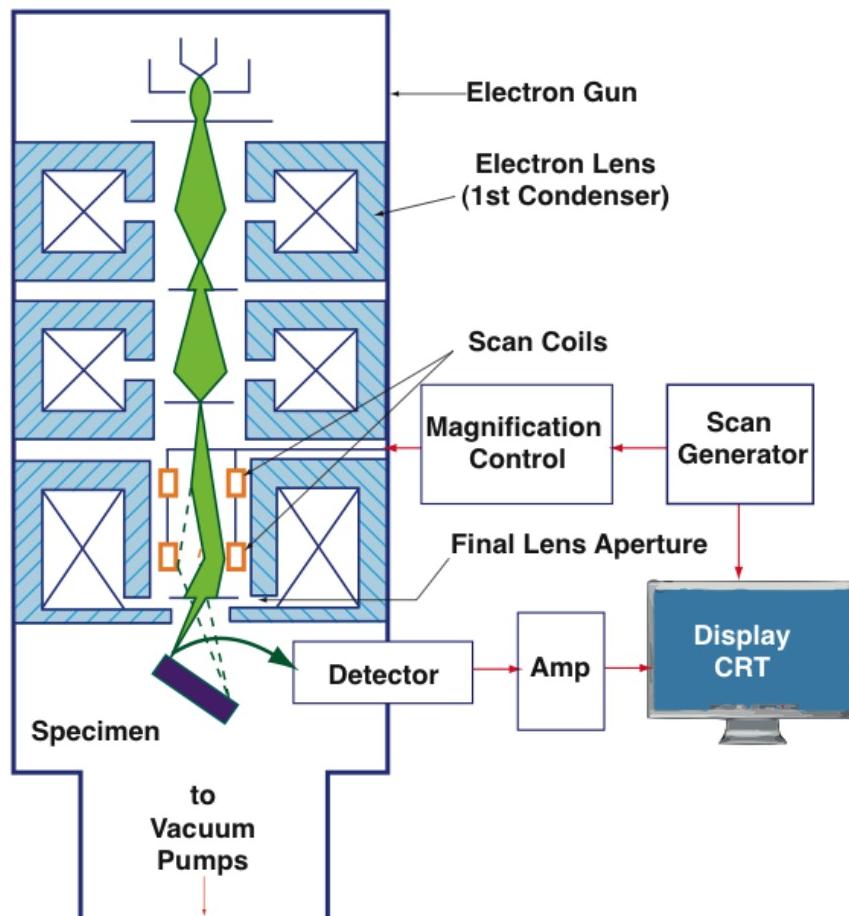


Figure 3.4. Working principle of FESEM

3.4. Energy Dispersive X-Ray Spectroscopy

Energy Dispersive X-ray Spectroscopy (EDX or EDS) is used to analyse the chemical composition of the materials. EDS is attached to the FESEM instrument therefore we can analyse surface morphology and chemical composition at a same time. The method is non-fatal [50]. EDX is required and

also important because analysing the chemical composition we can also study that if there are any contaminations in the processed film or not. Carbon is present in all types of films, so it is considered as universal contaminant. And also by EDX or EDS we can get the percentage of the materials present in it. For example, if we deposit ZnO in a substrate we can get the percentage of Zn, O and other materials if present in it. EDS works by finding the X-rays that are originated by a sample located in an electron beam. The electron beam energies the atoms in the sample that consequently generates X-rays to parole the exuberant energy. The intensities of X-rays produce peaks in the form of spectrum. Electron beam can admit over a specified area of the sample to investigate the composition in that area [1].



Figure 3.5. Field emission scanning electron microscopy at CSIR-NPL.

So, FESEM and EDS or EDX can be processed at the same time and very important to know the synthesized data and it's nanostructure for better characterization data.

3.5. Photoluminescence (PL)

Photoluminescence spectroscopy, normally referred to as PL, is when light energy, or photons, stimulates the emission of a photon from any matter. Photoluminescence spectroscopy is a contactless, non-destructive method to probe the electronic structure of the materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation [52]. The photo-excitation causes the material to jump to a higher electronic state, and will then release energy

or photons as it relaxes and returns to a lower energy level. One way this excess energy can be dissipated by the sample through the emission of light, or luminescence. The emission of light or luminescence through this process is photoluminescence, PL.



Figure 3.6. Photoluminescence spectroscopy at CSIR-NPL.

Now, Photoluminescence is divided into two categories: fluorescence and phosphorescence.

Fluorescence

When the chemical substrate undergoes internal energy transitions before relaxing to its ground state by emitting photons, some of the absorbed energy is dissipated so that the emitted light photons have lower energy than those absorbed. One of such most familiar phenomenon is fluorescence and it has a short lifetime of 10^{-8} s to 10^{-4} s.

Phosphorescence

Phosphorescence is a radiational transition, in which the absorbed energy undergoes intersystem crossing into a state with a different spin multiplicity. The lifetime of phosphorescence is usually from 10^{-4} to 10^{-2} s, much longer than that of Fluorescence [53].

Applications of PL

- PL spectroscopy is not considered a major structural or qualitative analysis tool, because molecules with subtle structural differences often have similar fluorescence spectra.
- It is used to study chemical equilibrium and kinetics
- It is important for various organic-inorganic complexes.
- It can track bio-chemical reactions.
- It can measure local friction (micro-viscosity) [54].
- It can track solvation dynamics.
- It can measure distances using molecular rulers: fluorescence resonance energy transfer (FRET).
- It can calculate band gap of semiconductors [55].

3.6. Raman Spectroscopy

Raman Spectroscopy is a non-destructive chemical analysis technique which provides detailed information about chemical structure, phase, crystallinity and molecular interactions. It is based upon the interaction of light with the chemical bonds within a material. This technique is also used to observe the vibrational, rotational, and other low frequency modes in a system. This technique is based on inelastic scattering also known as Raman scattering of monochromatic light usually from a laser in the visible, near infrared or ultraviolet range. And this Raman scattering was discovered by Dr. C.V. Raman and Dr. K.S.Krishnan in 1928 [56].

According to the law, when monochromatic radiation is incident upon a sample then the light will interact with the sample. It may be reflected, absorbed or scattered in some manner. And this scattering gives the information about molecular structure of the sample. Now, if the scatter energy is observed by means of a spectrometer, the bulk of the energy is found at the same frequency of the incident light. But a small

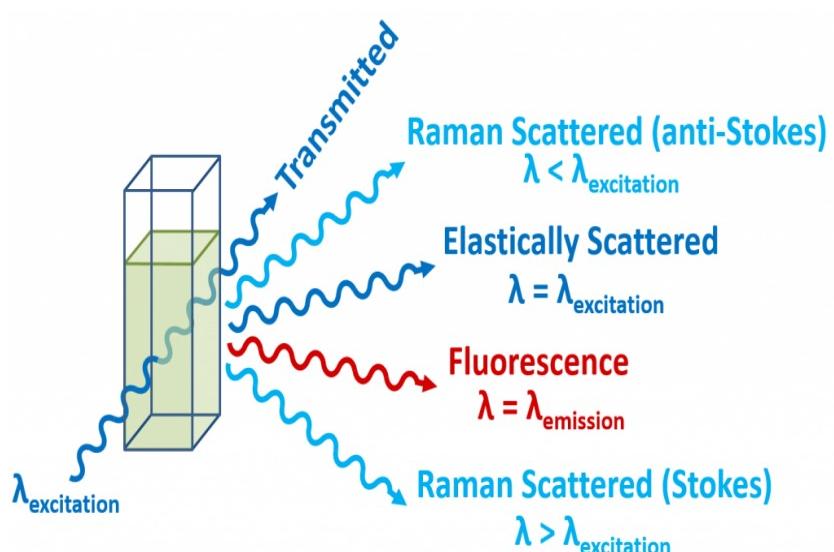


Figure 3.7. Raman scattering phenomenon.

portion of the scattered energy can be found at the different frequency. The first one is known as ‘Rayleigh scatter’ if no change is observed, or if it is elastically scattered. And the small portion which is inelastically scattered is known as ‘Raman scatter’, which can be described by 2 ways: 1. Stoke portions, 2. Anti-stoke portions.

Stokes portion

The material absorbs energy and the emitted photon has a lower energy than the absorbed photon that is called Stokes Raman scattering.

Anti-stoke portion

The material losses energy and the emitted photon have a higher energy than the absorbed photon that is called Anti-Stokes Raman scattering [57].



Figure 3.8. Raman spectrometer (Renishaw) at CSIR-NPL

In Raman spectroscopy, by varying the frequency of the radiation, a spectrum can be produced, showing the intensity of the exciting radiation for each frequency. The spectrum will show which frequencies of radiation have been absorbed by the molecule to raise it to the higher vibrational energy states. Now absorbing the photons it will be excited and forced to vibrate and move. We can also measure the vibrations [58]. The energy of a vibrational mode depends on molecular structure and environment.

Atomic mass, bond order, molecular substituents, molecular geometry and hydrogen bonding all affect the vibrational force constant which, in turn dictates the vibrational energy.

So, finally we can say that we can determine the nature of chemical bonds and symmetry of molecules of the sample. We can also determine the crystallographic orientation of the sample. And, as it is a non-destructive way to characterize a sample, so after this characterization we can still use the sample for further studies.

CHAPTER-4

RESULTS AND DISCUSSION

4.1. Introduction

ZnO material synthesised via thermal CVD was characterized for their structural, morphological and optical emission properties using various techniques such as x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive x-ray analysis (EDX), Raman scattering and photoluminescence (PL). The gas sensing characteristics of ZnO were also studied for the detection of CO gas molecules. The obtained results and the related discussion are presented in this chapter.

4.2. X-ray Diffraction (XRD)

After the deposition by thermal CVD, we obtained white-coloured film deposition on all substrates such as alumina, sapphire (0001), Si (111) and Ni. To examine their crystalline properties, the deposited films on alumina and sapphire substrates in the temperature range of 600~700 °C were subjected to XRD measurement at room temperature

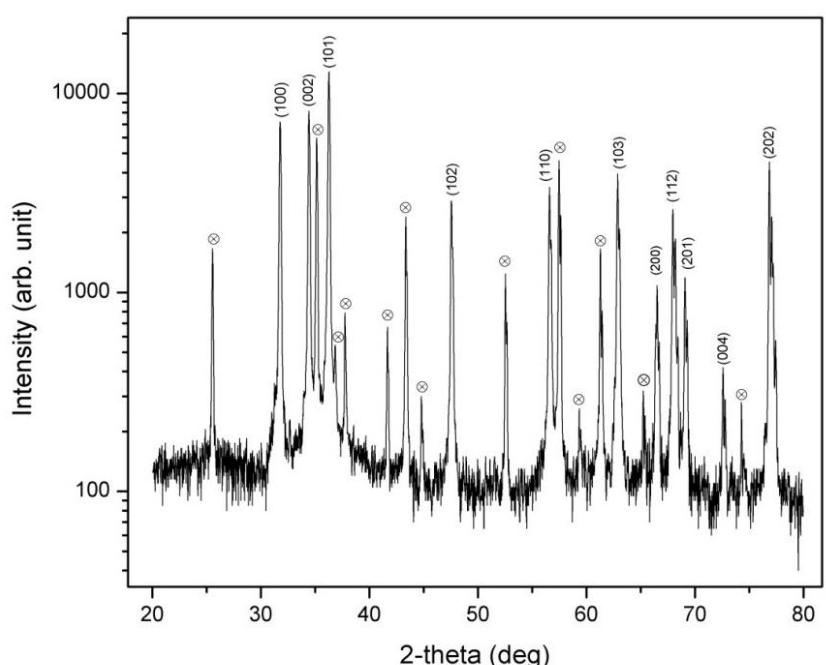


Fig: 4.1. XRD spectrum of ZnO film deposited on Alumina substrate.

using Cu K α_1 , having a wavelength $\lambda = 1.54060$ nm. It was observed that all the samples exhibited similar XRD pattern irrespective of the deposition temperature and substrate excluding the substrate related peaks. The typical XRD spectrum of ZnO deposited on alumina substrate is given in Fig. 4.1. We compared the output data with the JCPDS data of Card number- 80-0075, which corresponds to ZnO.

The obtained XRD peaks were closely matching with the ZnO reference data. In Fig. 4.1, the peaks are indexed by the (hkl) planes of ZnO and the XRD peaks correspond to pure alumina substrate are indicated by ‘ \otimes ’ symbol. The XRD data confirmed that the synthesized material is polycrystalline ZnO and has a hexagonal Wurtzite structure. Expect the ZnO and alumina XRD peaks, no peaks related to unreacted zinc or any impurity were observed indicating the high purity of deposited ZnO films [31]. The lattice constants i.e. ‘a’ and ‘c’ have been calculated from the XRD peak position using the equations described in Chapter 3 and are listed in table 4.1 for different deposition temperatures and substrates. The calculated lattice constant values are in close agreement with the reported data.

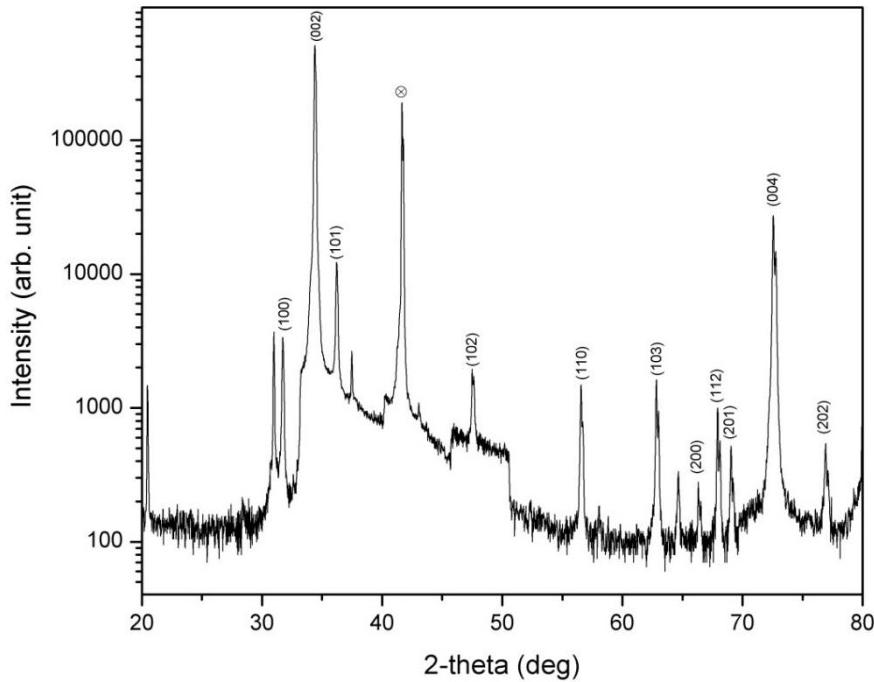


Fig: 4.2. The typical XRD spectrum of ZnO film deposited on sapphire (0001) substrate.

The typical XRD spectrum of ZnO film deposited on sapphire (0001) substrate is also shown in Fig. 4.2. The results obtained are similar to that of ZnO deposited on alumina substrate. Here, instead of

alumina peaks, a peak corresponding to sapphire (0006) plane is obtained as indicated by ‘ \otimes ’ symbol. The corresponding calculated lattice constants are also listed in the Table 4.1, which are in good agreement with rest of the data. Thus, from XRD measurements, the deposition of well-crystallized, single phase ZnO polycrystalline films on both alumina and sapphire substrates are confirmed [59].

Table: 4.1. Comparison of lattice constants of ZnO on alumina and sapphire substrates deposited at 600 and 700 °C

Lattice constant	JCPDS reference data	ZnO on Alumina		ZnO on Sapphire	
		600 °C	700 °C	600 °C	700 °C
a (Å)	3.2539	3.241	3.238	3.24	3.238
c (Å)	5.2098	5.2	5.18	5.19	5.18

4.3. Field Emission Scanning Electron Microscopy (FESEM)

The surface morphology of ZnO films deposited on alumina and sapphire substrates at various temperatures were analysed using FESEM images. The plane-view FESEM images of ZnO films deposited on alumina substrate at 600, 650 and 700 °C are presented in Fig.4.3. Analysing the SEM data, it is observed that ZnO films consist of various types of densely-packed nanostructures by varying the deposition temperature. For the ZnO prepared at 600 C, star-shaped nanostructures with needle-like arms are obtained. The nanostructures are laterally well connected by forming a network structure with high porosity. The length of the needle-arm is estimated to be 2.69 μm and the width of star-shape to be 448 nm. When the deposition temperature rose to 650 °C, the needle-like arms are becoming thicker making the film to appear as densely-packed star-shape with nanorod-arm network structure with moderate porosity. The length of the nanorod arm is found as 2.7 μm . The ZnO nanostructures deposited at 700 °C on alumina substrate is given in Fig. 4.3 (c). As seen, here, well-ordered, inter-connected nanorod network structure with high porosity is observed. The average length of the nanorod is observed to be 3 μm . The connected network is essential for lateral electrical conductivity and the films can be used for the fabrication of chemiresistive solid-state gas sensors. The large aspect ratio, i.e. surface-to-volume ratio

and high porosity of the obtained nanostructures are highly preferable for gas sensing applications since the gas sensing is predominantly a surface-bound phenomenon. Using EDX measurement attached to FESEM instrument, the ZnO is characterized to be stoichiometric.

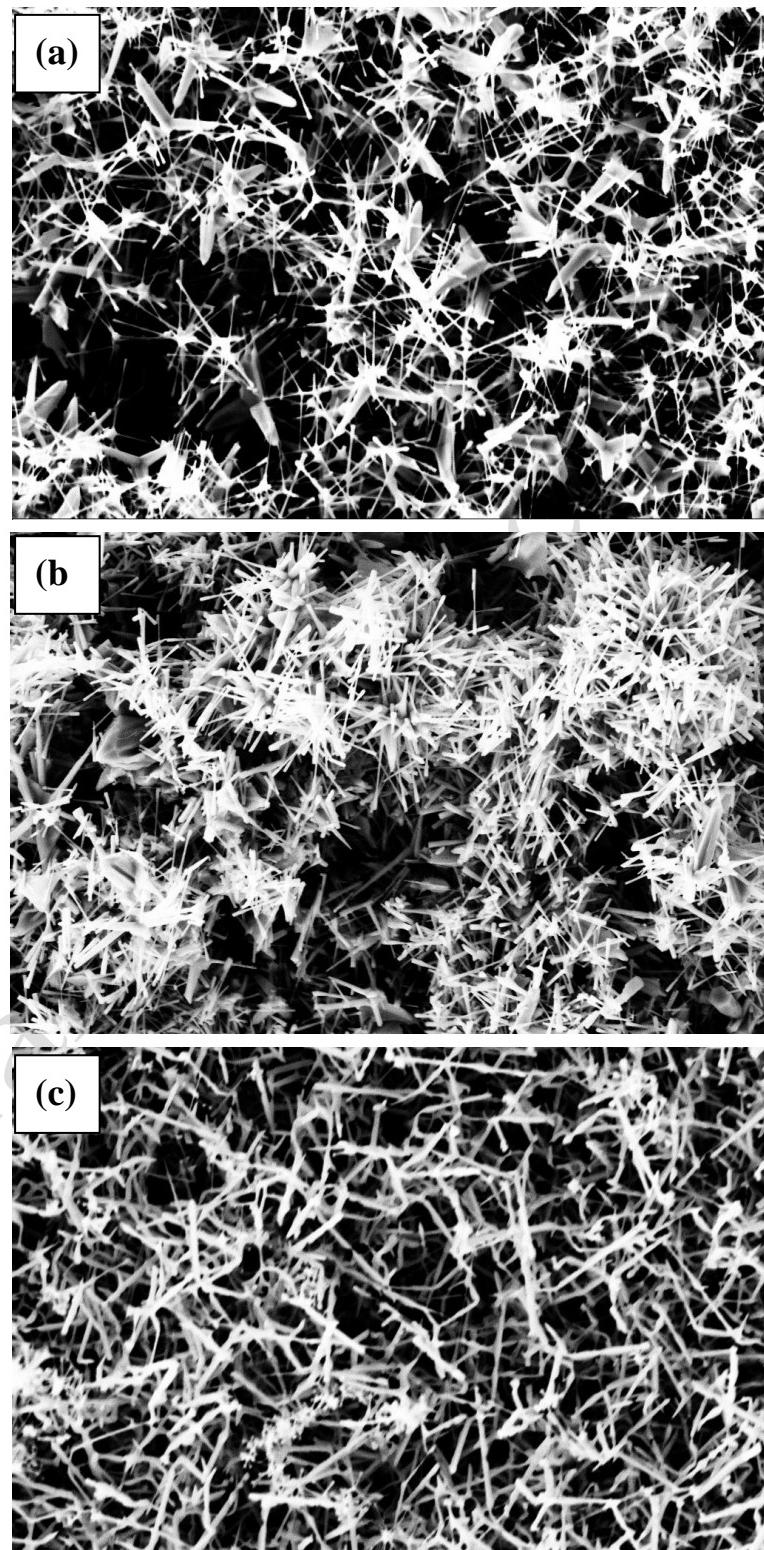


Fig: 4.3. Plane-view FESEM images (Magnification 10000 X) of thermal CVD deposited ZnO nanostructures on alumina substrate at (a) 600, (b) 650 and (c) 700 °C.

Table: 4.2. FESEM data analyses of ZnO nanostructures deposited on alumina and sapphire (0001) substrates at different temperatures

Substrate	Deposition Temperature	ZnO Morphology	Dimensions	
Alumina	600 °C	Star-shaped with needle-like arm structure, Low dense, Connected network, Highly porous	Nano needle-arm length ~2.69 μm	Star-shape width ~448 nm
	650 °C	Star-shaped with nanorod-like arm structure, Highly dense, Connected network, Moderately porous	Nanorod-arm length ~2.71 μm	Diameter of rod tip~100 nm
	700 °C	Well-interconnected nanorod network structure, Highly dense, Highly Porous	Nanorod length ~3.5 μm	Diameter of rod ~100-150 nm
Sapphire	600 °C	Vertically aligned nanorods, Low density, star-needle on top surface	Needle length on top surface ~3.26 μm	Diameter of rod ~100 nm
	650 °C	Vertically aligned nanorods, Low density, star-nanorod on top surface	Nanorod length on top surface ~3.88	Diameter of rod ~100-250 nm
	700 °C	Vertically aligned nanorods, High density, some Nano needles on top surface	Nanorod length on top surface ~5.18	Diameter of rod ~100-200 nm

In case of ZnO deposition on sapphire (0001) substrate, the plane-view FESEM morphologies of nanostructures obtained at different temperatures are shown in Fig. 4.4. In contrast to alumina substrate, here, growth of vertically well-aligned nanorod array is observed. In addition, a secondary growth of star-like nanostructures is seen on the top of the aligned nanorod array. The density of aligned nanorod increased significantly with deposition temperature and a tightly-packed nanorod array is achieved at 700 °C. The vertical alignment of ZnO on sapphire (0001) could be associated to the structural matching

between the two materials as well as the single crystalline nature of the sapphire substrate. In both ZnO on alumina and sapphire substrates, the increase dimension and density of the nanostructures with increasing deposition temperature could be understood based on the increased flux rate at higher deposition temperatures.

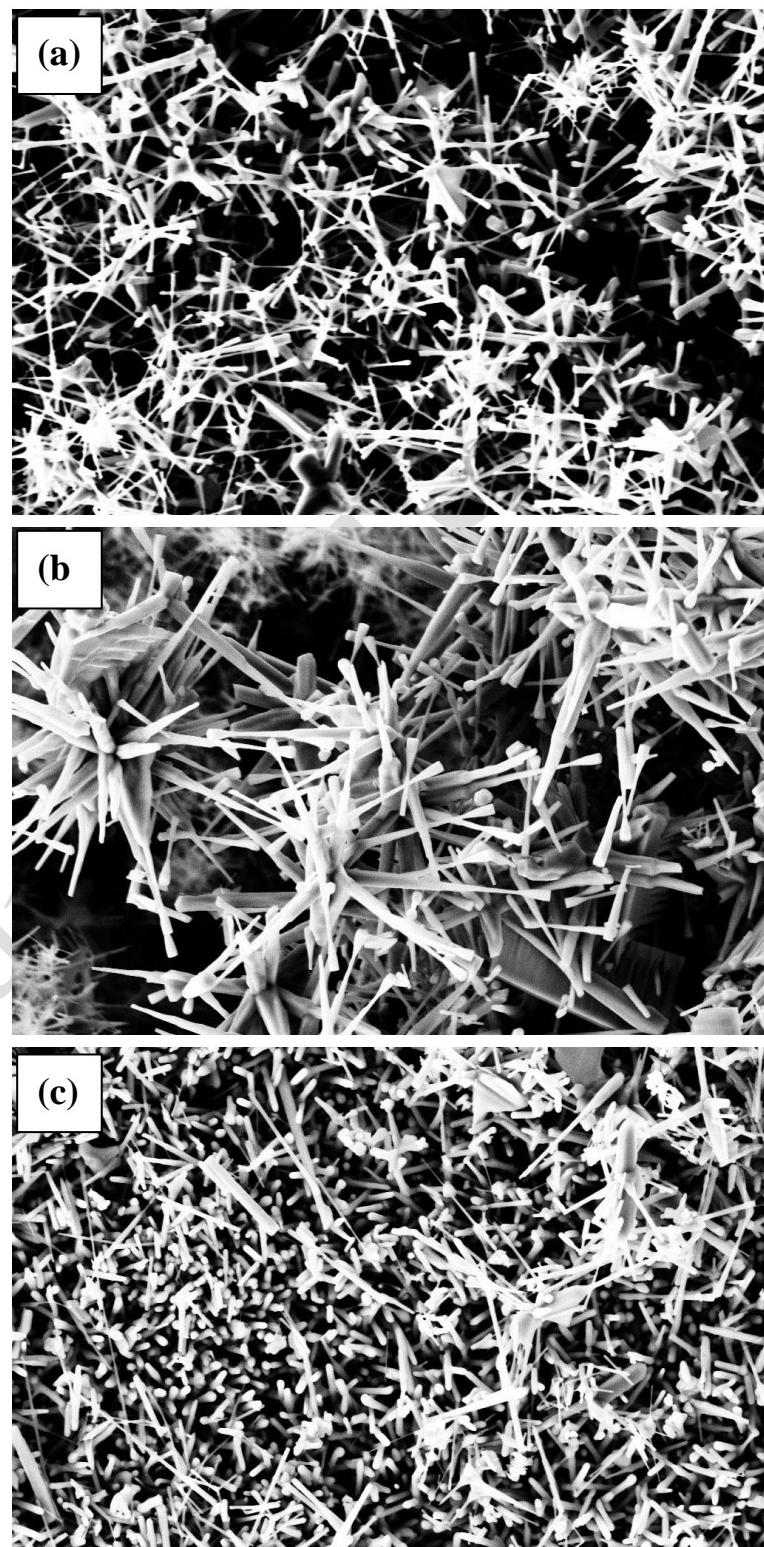


Fig: 4.4. Plane-view FESEM images (Magnification 10000 X) of thermal CVD deposited ZnO nanostructures on sapphire (0001) substrate at (a) 600, (b) 650 and (c) 700 °C

4.4. Raman Spectroscopy

The structural properties of deposited ZnO microstructures were also characterized by Raman scattering spectroscopy at room temperature in the range of 200–800 cm⁻¹ with a 514.5 nm laser line as excitation source. The typical Raman spectrum of ZnO deposited on Si substrate is shown in Fig. 4.5. From the figure, it is noticed that the E₂ (high) Raman mode of ZnO appears at 437 cm⁻¹ indicating the hexagonal Wurtzite structure of ZnO nanostructures [60]. The high intensity and narrow width is a result of good structural quality of the deposited material. In addition to ZnO, the Raman modes obtained at 302 and 521 cm⁻¹ are assigned to the Si substrate.

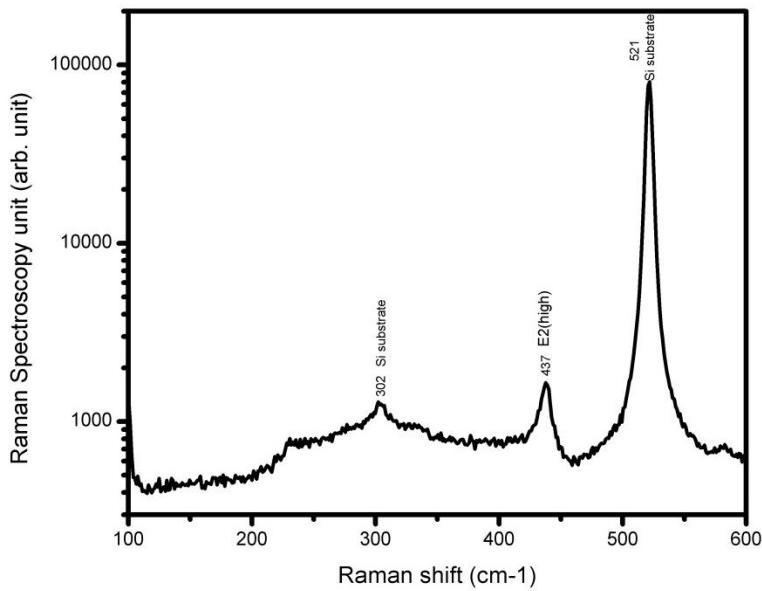


Fig: 4.5. Thermal CVD deposited ZnO nanostructure over Si substrate at 700 °C.

4.5. Photoluminescence (PL)

Optical emission properties of the grown ZnO nanostructures over alumina and sapphire (0001) substrates were measured at room temperature PL in the wavelength range of 350–600 nm using an

excitation wavelength of 325 nm of He-Cd laser. The features of PL spectrum of ZnO nanostructures deposited on alumina substrate were mostly similar for all the growth temperatures i.e. 600, 650 and 700 °C. The typical PL spectrum of ZnO deposited on alumina is presented in Fig. 4.6. The PL spectrum of ZnO nanostructures clearly showed an intense UV emission peak positioned around 383~384 nm with a full width at half maximum of about 14.5 nm. The UV emission peak is associated with near-band edge (NBE) emission of ZnO. The defect-related deep band emission around 500 nm is found to be very weak. The strong NBE emission due to band-to-band transition in the ZnO material along with negligible deep band emission reveals that the prepared ZnO nanostructured films have high structural and optical quality [61]. In case of ZnO on sapphire substrate, a similar strong UV emission is obtained at 383~835 nm wavelength region along with defect band emission around 500 nm at a considerable intensity level. The defect band intensity decreased drastically when the growth temperature increased from 600 to 700 C and also, the FWHM of near band-edge emission slightly decreased, i.e. from 16.1 to 14.4 nm, indicating an improvement in the structural properties of the ZnO nanorod array on sapphire substrate.

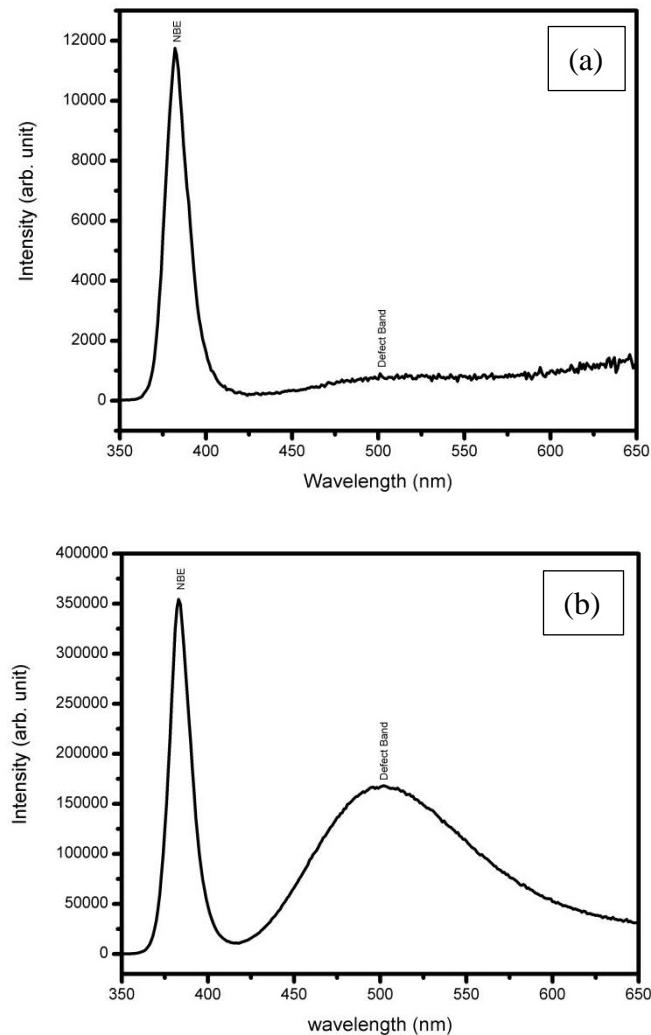


Fig: 4.6. Room temperature PL spectra of ZnO nanostructures deposited on (a) alumina and (b) sapphire (0001) substrates at 650 °C.

The data analyses of PL emission properties of thermal CVD grown ZnO nanostructures are summarized in Table 4.3. It is noted that the optical properties of ZnO nanostructure deposited at 700 °C have shown a comparable behaviour on both substrates.

Table 4.3. Room temperature PL analysis of ZnO nanostructures deposited on alumina and sapphire (0001) substrates.

PL peak	ZnO on Alumina			ZnO on Sapphire		
	600 °C	650 °C	700 °C	600 °C	650 °C	700 °C
Centre (nm)	383.53	383.10	384.61	385.12	385.09	383.95
FWHM (nm)	14.89	14.36	14.40	16.06	14.6	14.36

4.6. Gas sensing characteristics of ZnO nanostructures

The detailed characterization revealed the good crystallinity, morphology and other physical properties of ZnO nanostructures deposited by thermal CVD. After that, we used the ZnO nanostructures to test gas sensing characteristics using CO gas as the target gas.

In the chapter 1, we have already discussed the mechanism of a metal oxide semiconductor gas sensor. For the practical use of gas sensors, the thin films are placed in a plate type structure or sample holder, under which a heater is connected for measurement temperature variation, obviously the deposited side must be on the upper side so that it is in contact of air. Now, 2 probes which are used to calculate the resistance are connected on the deposited area using silver paste. Now the whole sample is placed inside a chamber which is separated from outside air. So that when we insert a gas of specific concentration, the

concentration must not be lowered by coming in the contact of environmental air. And the probes are connected to the measuring instruments which calculate the resistance. During measurement, a constant voltage is applied to the sample, for that a current source also forms in the circuit. The instrument measures the current primarily using the programming which is already set up in that instrument, and automatically calculates the resistance by following the Ohm's law. When a target gas is allowed to flow into the chamber and comes in contact with the thin film surface, a drop/increase of resistance is observed depending on the type of gas and semiconductor.

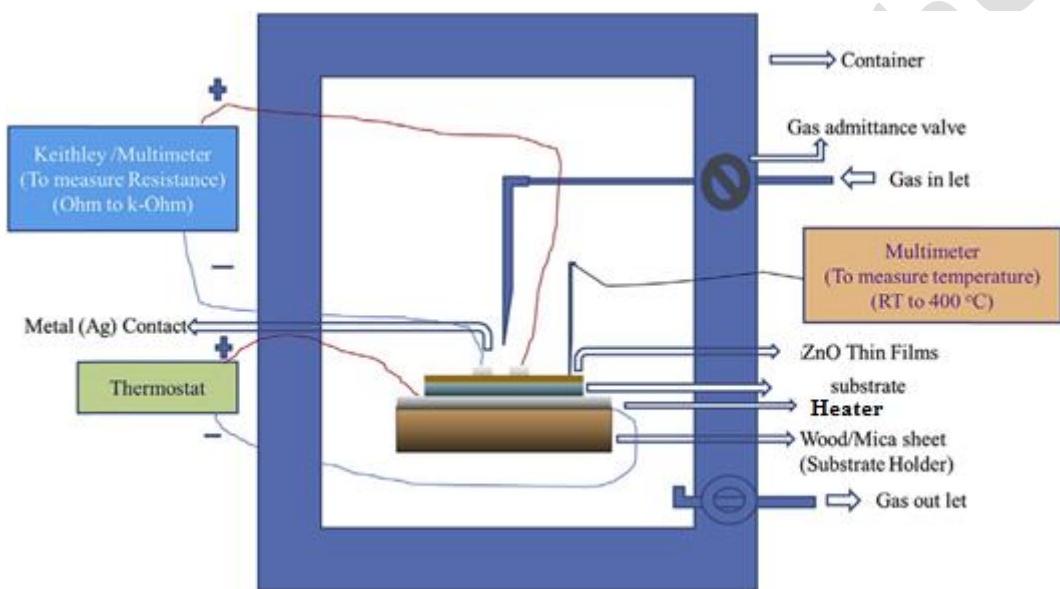


Fig: 4.7. Schematic diagram of a typical gas sensing set-up.

The gas sensing performance of metal oxide thin film is characterized mainly by the following four important parameters: Resistance drop, Sensitivity, response time, recovery time and selectivity etc. can be defined by this process.

4.6.1. Resistance drop (ΔR)

When the gases are passed through the surface of the thin film, the resistance change will occur for that film. The difference between the resistance in air (R_A) and the resistance in the gas (R_G) is called the resistance drop and is denoted by ΔR .

$$\text{So, } \Delta R = R_A - R_G$$

4.6.2. Sensitivity

Sensitivity is the percentage of the ratio of the resistance drop to the actual resistance in air. It is denoted by ‘S’. The S for the detection of reduction gas (e.g. CO gas) using a n-type semiconductor (e.g. un-doped ZnO) is calculated using the following equation.

$$S = \frac{\Delta R}{R_A} * 100\%$$

4.6.3. Response Time

Response time is defined by the time taken by the film to decrease 90% drop of the actual resistance in air (R_A) to the resistance in the presence of the target gas.

4.6.4. Recovery time

Same as the response time, recovery time is also taken as the time taken by the film to increase from its resistance in gas to the 90% increase of the resistance after removing the gas, i.e. in air.

4.6.5. Selectivity

Selectivity of a sensor is the quality of being sensitive to a particular gas in an ambient which contains multiple gases.

We tested the ZnO nanostructures deposited on alumina substrate at 600 C for the target gas of CO. We used a CO gas cylinder of 915 ppm concentration (uncertainty 1%) prepared by the gas metrology unit of CSIR-NPL. The CO concentration for sensing measurement was diluted to a concentration of 457 ppm using dry air. The gas sensing measurement was performed at difference temperatures such as 300 and 350 °C. The electrical contacts to the sample were made with Ag paint and the sample was loaded on the heater in the gas sensing chamber.

Initially, the chamber was evacuated using a vacuum pump to remove the ambient air and the filled with dry air. The sample temperature was increased to a designated value and was maintained at that temperature until the sample resistance was stabilized under the constant flow of dry air. For sensing measurement, the CO gas was admitted into the sample and the sample resistance was continuously

monitored using a computer program. A drop in resistance was observed in the presence of CO gas as shown in Fig. 4.8. Once the sample temperature is stabilized the CO gas flow was stopped and only the dry air was passed over the sample. The recovery of the sample resistance was observed as a function of time. This resistance measurement under CO ON and OFF conditions was repeated for few cycles and different measurement temperatures.

The sensing parameters such as sensitivity, response time and recovery time of the ZnO nanostructures measured at 300 and 350 °C are given in Table 4.4. A sensitivity of 6.5 % is obtained at 300 °C but increased to 17.6% when the measurement temperature rose to 350 °C. The increase in sensitivity at higher temperature can be understood as follows. At lower temperature, the ZnO surface is enriched with adsorbed oxygen in the oxidation state of O²⁻ but is gradually converted to have O⁻ at high temperature. The rate of chemical reaction between CO and O⁻ is comparatively more efficient, which leads to about 2.5 times hike in the sensitivity of CO sensing. The response time and recovery time are estimated to be about 28 and 68 s at 350 °C. Thus, the thermal CVD grown ZnO nanostructures on alumina substrate is shown to sense CO gas of concentration 457 ppm with a sensitivity of about 17.5 % within half a minute of time.

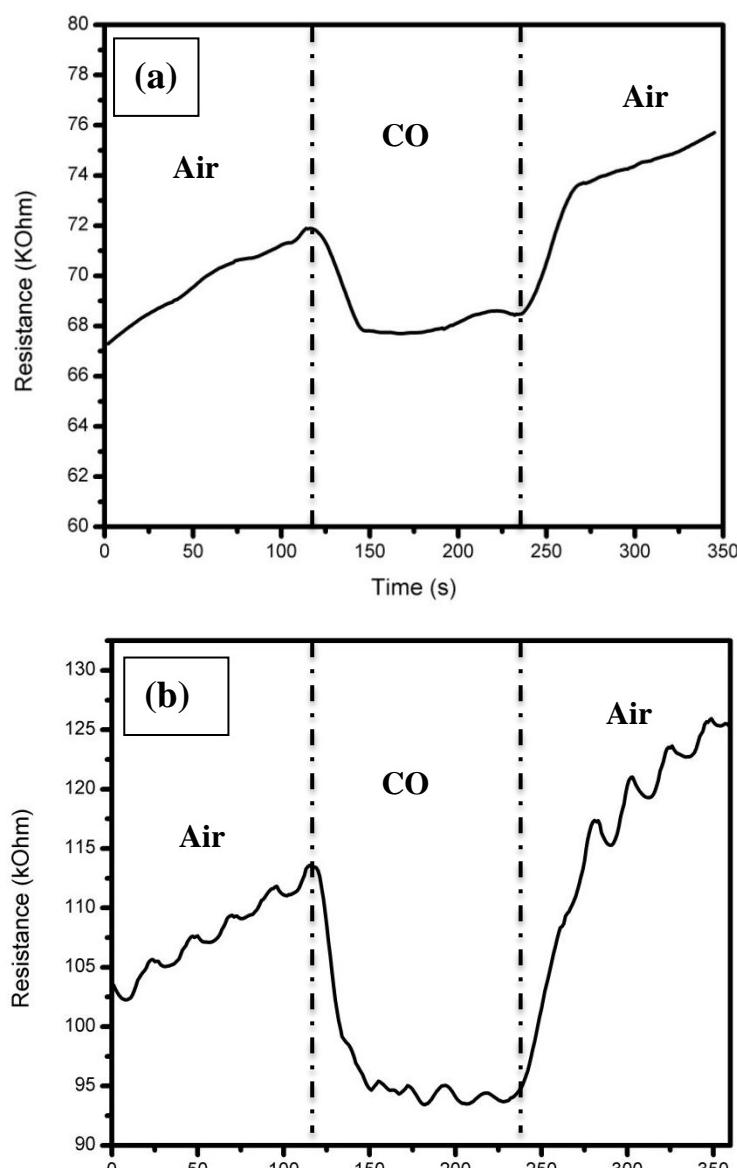


Fig: 4.8. Gas sensing characteristics of ZnO nanostructures for CO target gas measured at a temperatures (a) 300 and (b) 350 °C.

Table: 4.4. Comparison of Gas sensing properties of ZnO nanostructure at different measurement temperatures.

Measurement Temperature	300 °C	350 °C
CO gas concentration (ppm)	457	457
Resistance drop (ΔR) (Ohm)	4718	19979
Response time ($T_{Response}$) (sec)	13	28
Recovery time ($T_{Recovery}$) (sec)	61	64
Sensitivity (S) (%)	6.51	17.55

CHAPTER - 5

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

5.1. Conclusions

Collecting all the results of the characterization techniques like, we can conclude that the ZnO nanostructured thin films were successfully deposited on alumina, sapphire and Si substrates using thermal CVD technique. The physical properties of prepared ZnO nanostructures were characterized using various techniques such as XRD, FESEM, Raman Spectroscopy and PL. The effect of deposition temperature on the formation of ZnO nanostructures have been studied in the range of 600~700 °C.

By the help of XRD data, we compared the results with the theoretical values (JCPDS card no. 80-0025). XRD data confirmed that the deposited material is polycrystalline ZnO and has a hexagonal wurtzite structure. Except the peaks related to ZnO and substrates, no other peaks from unreacted zinc or any other impurity were observed indicating the high purity of prepared ZnO material.

Using the FESEM images, surface morphology of ZnO films deposited on alumina and sapphire substrates at various temperatures were analysed. And various types of well-ordered, inter-connected and vertically aligned nanostructure with high porosity have been observed on the alumina and sapphire substrates depending on deposition temperature. Raman spectroscopy data complimented the XRD results that the deposited material in the thin film form is the hexagonal Wurtzite structure of ZnO nanostructures.

From room temperature PL spectra, it is observed that the ZnO nanostructures grown on the substrates have a strong NBE emission due to band-to-band transition in the ZnO material. And a negligible deep or defect band emission is observed, especially the nanostructures prepared at higher temperature. This states that the prepared ZnO nanostructured films have high structural and optical quality.

Finally, the ZnO nanostructured films were examined for the gas sensing performance using 457 ppm of CO target gas. It has been observed that along with the increase in temperature, the gas sensing parameters such as sensitivity, response time, and recovery time were also improved. The CO sensitivity was increased from 6.51% to 17.55% when the temperature was raised from 300° C to 350° C. The

nanostructures exhibited a quick response and recover period below one minute. The results demonstrate that the ZnO nanostructured films deposited by thermal CVD process with high surface-to-volume ratio and surface porosity are highly suitable for gas sensor applications.

5.2. Suggestions for Future Work

- The sensitivity and selectivity of the ZnO nanostructure can be further improved by addition of metals and other metal oxides.
- As the metal oxide requires a higher operation temperature, a suitable sensor heater can be developed and attached to the sensing thin films for effective operation.
- Attempts can be made to fabricate a discrete gas sensor device with suitable integration of sensor electrodes and micro-heater for practical applications.

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